THE EFFECT OF A HYDROGEN PLASMA ON THE HYDRIDING OF TITANIUM: KINETICS AND EQUILIBRIUM CONCENTRATION

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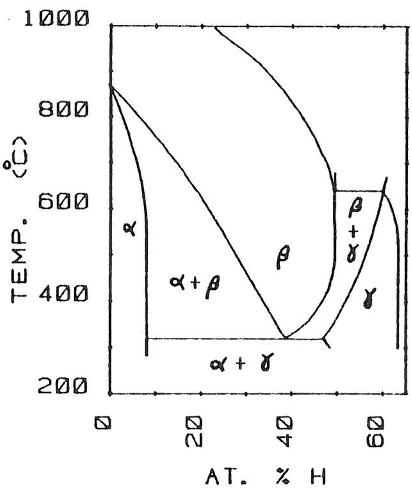
ABSTRACT

The interaction of titanium with hydrogen gas and with a hydrogen plasma was investigated. At a given sample temperature and gas pressure, the equilibrium concentration of hydrogen in titanium is reached over 10 times faster in the plasma hydriding case than in the H_2 hydriding case. For the latter the equilibrium concentration agrees well with the existing data; however, for the former, markedly higher hydrogen concentrations could be achieved. In addition, embrittlement of the plasma-treated samples occurred, with the appearance of cracks accompanied by a lowering of the hydrogen concentration in the samples. This decrease is explained in terms of localized plasma energy gradients within the cracks. Rutherford backscattering, ESCA, SEM and mass spectrometric thermal desorption measurements were used to characterize the samples. The implications of these results for controlled thermonuclear fusion devices are discussed.

1. INTRODUCTION

The establishment of research programs on controlled thermonuclear fusion has stimulated interest in plasma-surface interactions. The hydrogen plasma-titanium system merits particular attention because of titanium's importance as a structural material and as a vacuum getter in tokamak devices. Despite this importance there have been few studies reported, and consequently a great deal of reliance is placed upon an analogical comparison with the gas-metal system[1]. The basis of this comparison is uncertain and the need for a quantitative comparison of the interactions at various temperatures and pressures was the stimulus for the present study.

The phase diagram of the Ti-H_2 system (Fig. 1), although incomplete in the low temperature and low pressure region, is fairly well established[2,3]. The amount of hydrogen soluble in the metal depends upon the system's temperature and the gas pressure. However, it has been found both experimentally and theoretically that the hydrogen concentration in various metals subjected to either ion bombardment or a plasma discharge can be higher than the solubility of the gas in the metal[4-7]. That this phenomena can lead to embrittlement in the case of titanium may be seen by consideration of the phase diagram and studies on that subject. If the hydrogen in solution at an elevated temperature precipitates when the Ti-H alloy is cooled to near room temperature, where the solubility of hydrogen in the α and β phases is low or zero, the metal will be subject to impact embrittlement[8], while if it is retained in solution and precipitates under the influence of strain, low strain-rate embrittlement can occur[1,8]. This presents potential problems for controlled thermonuclear fusion devices which make use of titanium.

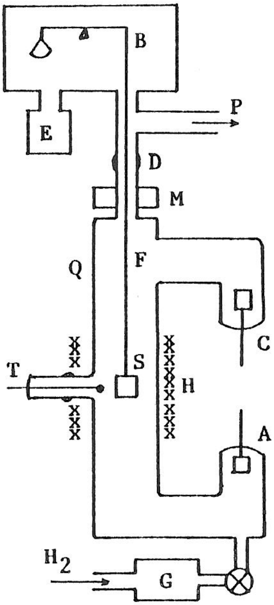


The aim of the present work is to establish the differences between the gas and the plasma interactions with titanium, both as regards the kinetics and the steady state hydrogen concentrations for these systems. The technique of in situ thermogravimetry was used to examine these interactions. In addition, surface analysis techniques (x-ray photoelectron spectroscopy and Rutherford backscattering), SEM and mass spectrometric thermal desorption studies were used ex situ to characterize the samples.

Fig. 1. The phase diagram of the Ti-H_2 system (after McQuillan[2]).

2. EXPERIMENTAL APPARATUS AND PROCEDURE

The time-dependent hydrogen concentration in the sample was calculated from the weight increase due to hydriding which was measured continuously in situ by means of a technique developed at our laboratory earlier and described elsewhere[9,10]. Because of the strict requirements on the purity of hydrogen during the hydriding experiments, a bakeable UHV system, a schematic of which is given in Fig. 2, was used in the present study. The titanium sample, S, was suspended from the balance, B, by a quartz fiber, F, and floated electrically in the positive column of a DC discharge (with electrodes at A and C) contained in a quartz tube, Q. The tube was connected to the balance chamber and the pumping system at point D; a magnet, M, prevented the discharge from reaching the metal part of the system. A thermocouple, T, whose junction was covered with a piece of titanium was used to measure the temperature. Hydrogen was purified using a palladium permeation cell, G. An external heater, H, was used to maintain the sample at the desired temperature.



The change in mass of the sample was measured using a Cahn electrobalance (UHV model) which was enclosed in a temperature-stabilized housing. The neutral gas pressure was measured using an MKS Baratron capacitance manometer, E. The sample's temperature could be controlled to within ±2°C and the gas pressure to within ±0.005 torr of the values desired. Using the appropriate mass

Fig. 2. Schematic of the experimental apparatus. (For details see text.)

range, mass changes could be resolved to better than 10^{-2} mg, which corresponds to an absolute error of less than 0.1 at. % of hydrogen in TiH_2.

The system was pumped by a turbomolecular pump. During a hydriding run it was pumped by a rotary pump fitted with a Zeolite molecular sieve. The base pressure was 10^{-8} torr, and a quadrupole mass spectrometer gas analyzer indicated that the major impurities present were H_2 and H_2O.

The samples, 99.7% pure titanium sheets with a thickness of 0.25 mm and a cross section of 2 cm^2, were etched in a 5% HF + 5% H_2O_2 aqueous solution and rinsed with distilled water and alcohol. Some were also annealed at 1000°C under UHV. The system was discharge cleaned for several hours before each experiment. Samples were inserted and removed under an argon atmosphere using a glove bag technique. The thermocouple caps were changed for each run. After pumping the system down to around 10^{-7} torr the sample was heated to the desired temperature and hydrogen was introduced into the tube.

3. RESULTS AND DISCUSSION

Kinetic studies of the titanium-hydrogen plasma (Ti-plasma) interaction show that the hydrogen concentration in the samples passes through a maximum (Fig.3, curve a) and then decreases to a steady state value. For the corresponding interaction of titanium with molecular hydrogen (Ti-H_2) the concentration monotonically approaches a final equilibrium value (curve b). Quantitative mass spectrometric thermal desorption measurements and Rutherford backscattering spectroscopy (RBS) confirmed that the measured weight changes were the result of hydrogen absorption. Table 1 lists the maximum and steady state concentrations of hydrogen for both interactions under two experimental conditions. These results represent data from about 30 experimental runs and the

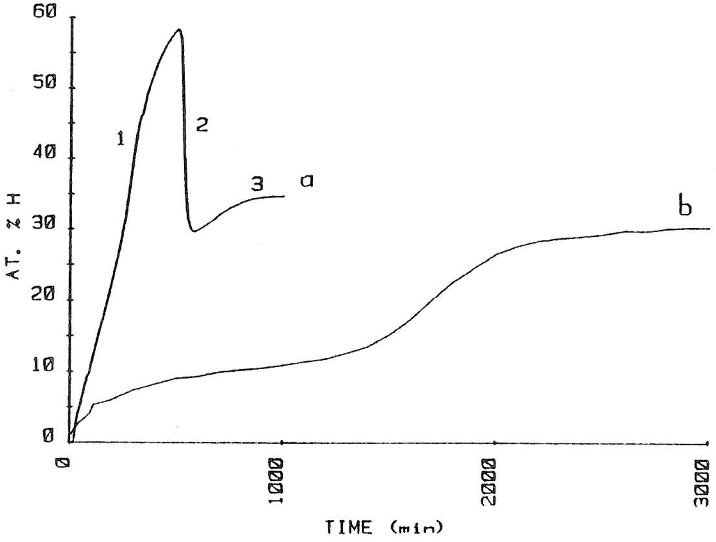


Fig. 3. Hydrogen concentration in titanium samples plotted against exposure time for (a) plasma hydriding and (b) gas hydriding. For the former, absorption, desorption and steady state regions are denoted by 1, 2, and 3, respectively. (Experimental conditions: 450°C, 0.465 torr)

Table 1. Steady State and Maximum Hydrogen Concentrations (at. %)

Hydrogen Pressure (torr)	0.465 ± 0.005	0.200 ± 0.005
Sample Temperature (°C)	450 ± 2	475 ± 2
Maximum Concentration (plasma)	56.4 ± 2.0	53.1 ± 5.9
Steady State Concentration (plasma)	30.9 ± 3.2	32.4 ± 5.2
Steady State Concentration (gas)	30.4 ± 2.6	6.2 ± 0.3
Equilibrium Concentration (gas)[2,3]	36.3	6.2

errors in concentration are a measure of the statistical errors only. At 450°C and 0.465 torr the reported equilibrium concentration of hydrogen is 36.3 at. %, indicating that the titanium is in the β phase, whereas at 475°C and 0.2 torr the equilibrium concentration is 6.2 at. %, with the metal in the α phase[2,3]. The steady state concentrations found for the Ti-H_2 interaction are in reasonable agreement with these values. In contrast, the maximum hydrogen concentrations found for the Ti-plasma interaction are markedly higher, with the titanium entering the γ phase. In one series of experiments the titanium was exposed to molecular hydrogen under conditions at which only a low solubility (6.2 at. %) of the gas in the α phase was expected. After equilibrium was achieved a discharge was initiated, and the metal began to rapidly absorb hydrogen and to form the γ phase hydride. These results clearly demonstrate that the Ti-plasma and Ti-H_2 interactions differ considerably.

The differences in the two types of interactions may be illustrated by considering the reaction mechanisms, which, for the Ti-H_2 case, may be expressed as

$$\mathrm{Ti} + \mathrm{H_2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ti\cdots H_2(a)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ti\cdots H(a)} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{TiH_x(s)}\ , \qquad (1)$$

where (g), (a) and (s) represent gaseous, adsorbed and solid states, respectively. In a single phase region the solubility of hydrogen in the metal is given by Sievert's Law[2]. However, for the Ti-plasma reaction the mechanism may be expressed as

$$\begin{tikzcd}
\mathrm{Ti} + \mathrm{H_2(g)} \arrow[r, shift left, "k_{4(p)}"] \arrow[rrd, shift right, "k_8"'] & \mathrm{Ti} + \mathrm{H(g)} \arrow[l, shift left, "k_{-4(p)}"] \arrow[r, shift left, "k_5"] & \mathrm{Ti\cdots H(a)} \arrow[l, shift left, "k_{-5}"] \arrow[r, shift left, "k_6"] \arrow[d, shift left, "k_{-7}"] & \mathrm{TiH_x(s)}\ , \arrow[l, shift left, "k_{-6}"] \\
 & & \mathrm{Ti\cdots H_2(a)} \arrow[u, shift left, "k_7"] \arrow[llu, shift right, "k_{-8}"'] &
\end{tikzcd} \qquad (2)$$

where (p) refers to the plasma state. The solubility of hydrogen in this case may be expressed as the ratio of the probability of penetration into the metal lattice (k_6) and the atom flux for the forward reaction to a phenomenological recombination coefficient and surface roughness for the reverse reaction[7]. The constants k_3 and k_6 may differ in the two interactions because different surface sites may be involved. The fact that higher hydrogen inventories than expected were achieved with the Ti-plasma interaction may be explained by the flux of atomic hydrogen to the surface. If the recombination is not dominant and if penetration into the solid proceeds at a reasonable rate (this point will be discussed later), then the atoms bypass the step of dissociation at surface sites, resulting in a surface coverage of atoms that can be achieved only in H_2 at a considerably higher pressure. The theoretical analysis of these processes is complex and data on the rate constants are not available.

At the point at which the hydrogen concentration is a maximum in the Ti-plasma runs cracks appeared in the samples concomitant with a decrease in sample weight and a slight increase in the gas pressure. Cracking of the samples occurs in the region where the body-centered cubic β phase is partially or totally transformed into the face-centered cubic γ phase. This point separates Region 1 of Fig. 3, curve (a), in which the hydrogen is being absorbed, from Region 2, in which it is being desorbed through the surfaces of the newly-formed cracks. The desorption is consistent with the presence of localized plasma energy gradients within the cracks[11]. SEM studies indicate that the larger crack widths were on the order of 20 μm, which is sufficiently small to produce predominantly molecular fluxes within the cracks. As a consequence of the high mobility of hydrogen in the metal[12] the new steady state concentration of hydrogen is determined by the balance between the absorption on the plasma-exposed surfaces and the desorption through the crack surfaces. This results in a hydrogen concentration in the titanium which approaches a new steady state value, as seen in Region 3. Small oscillations in the concentration which occur in this domain are not yet understood, and the influence of crack propagation and of the contamination of the crack surfaces needs further investigation.

A detailed kinetic study of over 30 samples indicates that the Ti-plasma hydriding is over an order of magnitude faster than the Ti-H_2 hydriding at 450°C and 0.465 torr. Investigations using both annealed and unannealed samples reveal no significant differences in the general form of Region 1 of Fig. 3, curve (a), for the Ti-plasma reaction; however, the form of Region 2 was more reproducible for the annealed samples. The rate of hydriding was generally faster for the annealed samples than for the unannealed ones.

The differences in rate for the Ti-H_2 and Ti-plasma reactions are inconsistent with a simple diffusion model[13] that assumes a clean surface with a constant surface coverage of H atoms, insofar as the predicted time taken to approach equilibrium is independent of the coverage. Under such circumstances, equilibrium should be reached in a time on the order of minutes. Thus, the rate-limiting step is not the diffusion of hydrogen in the titanium but, more likely, is due to surface contamination. The presence of a surface nitride layer has been shown to present a barrier to the absorption of hydrogen[14]. A study of the uptake of hydrogen by samples with oxygen and nitrogen present on the surface, made concurrently with this work on a different apparatus, shows a pronounced influence of the contaminant on the hydrogen uptake[15]. Figure 4 shows the x-ray photoelectron spectra of the titanium 2p core levels and satellite structures for pure metal (a), a plasma-hydrided sample (b) and a gas hydrided sample (c). It is readily seen that the hydrided samples undergo oxidation, and that the oxide layer is thicker for the gas-hydrided sample.

The α-β phase transition is another process which may influence the rate of hydriding. This manifests itself for the Ti-H_2 reaction (Fig. 3, curve (b)) where the rate of hydriding slows near the level of 8 at. % hydrogen. This behavior has also been observed for the Ti-plasma reaction, but rarely in such a pronounced manner. Thus the role of the structural reorganization and how it is induced may be of some importance as well.

4. CONCLUSIONS

Significantly higher inventories of hydrogen in titanium can be achieved for the interaction of the metal with a hydrogen plasma than normally would be expected from a consideration of the metal-gas interaction. Under the plasma conditions of these experiments the resulting hydrogen embrittlement led to crack formation in the samples. Caution should be exercised in the use of existing thermodynamic data for the Ti-H_2 system to predict the behavior of titanium in a hydrogen plasma. This point is of significance regarding materials selection in controlled thermonuclear fusion technology.

Kinetic studies indicate that the surface oxide layer, present on all samples, is the rate-limiting factor. Diffusion of hydrogen in the metal is relatively fast. However, the influence of the α-β and β-γ phase transitions on the absorption rate indicates that these processes may also be rate-determining in the phase transition regions of the reaction. The Ti-H_2 reaction proceeds at a lower rate than the Ti-plasma reaction.

The take-home lesson of this study is that "fusion may breed fissures, and fissures and fusion don't mix."

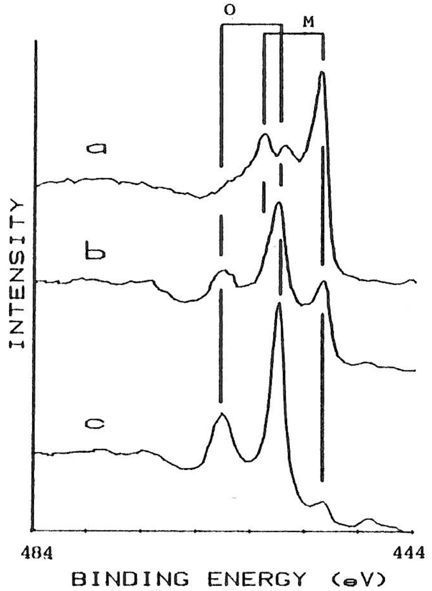


Fig. 4. Ti 2p XPS spectra for (a) an etched sample, (b) plasma-hydrided sample and (c) gas-hydrided sample. Metal and oxide contributions are denoted by M and O, respectively.

5. REFERENCES

(1) J.W. Davis and D.L. Smith, J. Nucl. Mater. 85, 71 (1979)
(2) A.D. McQuillan, Proc. Roy. Soc. 204, 309 (1951)
(3) P. Dantzer, O.J. Kleppa and M.E. Melnichak, J. Chem. Phys. 64, 139 (1976)
(4) G.M. McCracken, J. Nucl. Mater. 86, 943 (1979)
(5) G. W. Look and M.I. Baskes, J. Nucl. Mater. 86, 943 (1979)
(6) R. Behrisch, J. Nucl. Mater. 86, 1047 (1979)
(7) I. Ali-Khan, K.J. Dietz, F.G. Waelbroeck and P. Weinhold, J. Nucl. Mater. 86, 1151 (1979)
(8) W.M. Mueller, J.P. Blackledge and G.G. Libowitz, eds., Metal Hydrides (Academic Press, New York), p. 17, (1968)
(9) A.P. Webb and S. Vepřek, Chem. Phys. Lett. 62, 173 (1979)
(10) S. Vepřek and A.P. Webb, Proc. 4th Int. Symp. Plasma Chem, Zurich 1979, p. 79
(11) S. Vepřek, Pure & Appl. Chem. 48, 163 (1976)
(12) R.J. Wasilewski and G.L. Kehl, Metallurgica 50, 225 (1954)
(13) J. Crank, The Mathematics of Diffusion (Clarendon Press, Oxford), p. 53 (1975)
(14) C. Braganza, H. Stuessi and S. Vepřek, J. Nucl. Mater. 87, 331 (1979)
(15) To be published